film formed on the surface.

[0002]

[Prior Art]

Conventionally, a Ni-base brazing alloy specified in JIS (JIS Z3265) is mainly used for brazing of stainless steel, and is excellent also in oxidation resistance and corrosion resistance. Therefore, the alloy has been generally used for process of brazing stainless steal to produce various kinds of products such as a heat exchanger and a gas turbine.

[0003]

However, in recent years while a brazing is especially required which has a corrosion resistance under salt water environment and may be carried out at a temperature as low as possible, the conventional Ni-base brazing alloy has following several problems. Although the BNi-5 Ni-base brazing alloy containing Si specified in JIS has a good corrosion resistance and a heat resistance, it has a high liquidus of 1160°C so that it requires to be heated up to 1200°C for brazing, during which the property of the stainless steal would be decreased. Although BNi-1, 1A, 2, 3 and 4 containing B, and BNi-6 and 7 containing P have a low melting point and have an advantage of being brazed at a low temperature of about 1050°C, they have a difficulty in a corrosion resistance to

salt water etc.

[0004]

[Problems to be Solved by the Invention]

An object of the present invention is providing a Ni-base brazing alloy, the alloy brazed at a temperature as low as possible (approximately 1050°C) having an good wettability and, in particular, excellent corrosion resistance to salt water in the case where the alloy is used for brazing a metal to a metal and, in particular, in the case where it is used for brazing a stainless steel with a stable oxide film formed on the surface.

[0005]

[Means for Solving the Problems]

The present inventors newly reviewed a validity of each component of Ni-base brazing alloys defined in conventional JIS, further improved the component. And a research has been carried out to solve the problems mentioned above by building a new alloy composition in order to find a novel composition for Ni-base brazing alloy, with a good wettability between a stainless steel, that can be brazed at a temperature as low as possible in brazing the stainless steel with a stable oxide film formed on the surface, and that has an outstanding corrosion resistance especially to salt water

[0006]

Consequently, P and Si were chosen as melting point lowering elements based on nickel, and the alloy composition that has a required melting point was found out by limiting each amount, and the total amount of the P and Si. Furthermore, it was found out that salt-water corrosion resistance is improved by addition of Cr and Mo in a range not inversely affecting a melting point or a wettability etc. Accordingly, the Ni-base brazing alloy excellent in wettability and corrosion resistance of the present invention comprises Cr in an amount of 10 to 30 % by weight, P in an amount or 2 to 11 % by weight, Si in an amount of 1 to 10 % by weight, wherein the total amount of P and Si is 10 to 13 % by weight, and, if needed, Mo in an amount of no more than 5 % in weight, and a remainder of Ni and unavoidable impurities. As an unavoidable impurities, the total amount of no more than 7 % of all impurities is acceptable for Fe in an amount of no more than 5%, Co in an amount or no more than 1 %, Cu in an amount of no more than 1%, Mn in an amount of no more than 0.5 %, B in an amount of no more than 0.3%, C in an amount of no more than 0.15 %, with the total amount of no more than 0.5% of other elements.

[0007]

[Operation]

The reason why the range of each element was limited as in the above described paragraph, in the present invention, will be described below. The following term % is represented by weight %. Cr is effective as an element that may be solved into nickel to form a nickel-Cr solid solution so that an oxidation resistance, a heat resistance, and a corrosion resistance of the obtained alloy may be improved, and especially in the brazing alloy composition of the present invention a corrosion resistance to salt water is improved. However, in the case where the amount of Cr is less than 10 % the effect of improvement is limited and in the case where more than 30 % the wettability with stainless steel is decreased. According to the above described reason the amount of Cr is limited with 10 to 30 %.

[0008]

P and Si remarkably influence the melting point of the obtained alloy due to the eutectic reaction with the Ni-Cr solid solution, and as a result significantly influence the property relating to brazing and the corrosion resistance of the alloy. In the brazing alloy composition of the present invention the limitation of total amount of the elements P and Si may significantly influence the melting point of the obtained alloy. Thus, in case of the alloy having the total

content of P and Si of less than 10 % by weight, the obtained alloy tends to become hypo-eutectic to raise the temperature of the liquidus and to spread the width to the solidus so that it is difficult to be brazed efficiently. In case of the alloy having the total amount of P and Si of more than 13 % by weight, the obtained alloy becomes hyper-eutectic to raise the temperature of the liquidus so that the alloy is brittle. Thus the amount of P and Si cause action and reaction for the properties of melting point and the corrosion resistance.

[0009]

Therefore, each amount of P and Si is limited based on each balance of properties. When P is less than 2%, and when Si exceeds 10%, the melting point of the alloy is increased and it is impossible to be brazed at a predetermined temperature. Moreover, when Si is less than 1%, and when P exceeds 11%, the corrosion resistance and the strength of the alloy are decreased. According to the above described reason the content of P is limited with 2 to 11 %, Si with 1 to 10%, and the total of P and Si with 10 to 13%.

[0010]

The alloy composition of Ni, Cr, P and Si as described above has the good wettability and the corrosion resistance, and Mo can be added if needed since the corrosion resistance

is further improved with the addition of Mo. However, if the content of Mo exceeds 5 %, the effects will be decreased, a melting point will be increased, and as a result it becomes difficult to be brazed efficiently. The content of Mo is limited to no more than 5 % according to the above reason.

[0011]

Content of the following elements, although unavoidable, is acceptable as impurities that does not adversely affect on the wettability and the corrosion resistance in manufacturing a Ni-base brazing alloy of the present invention. As an unavoidable impurities, the total amount of no more than 7 % of all impurities is acceptable for Fe in an amount of no more than 5 %, Co in an amount or no more than 1 %, Cu in an amount of no more than 1%, Mn in an amount of no more than 0.5 %, B in an amount of no more than 0.3%, C in an amount of no more than 0.15 %, with the total amount of no more than 0.5% of other elements. The present Ni-base brazing alloy may be formed in powder, which is generally prepared by an atomizing method, and formed into a foil or a rod.

[0012]

[Embodiments of the Invention]

Typical examples according to the present invention and controls out of the present invention will be shown as follows.

[Example]

Alloy compositions, melting points, and the result of brazing test and salt water spray test for the piece of a brazing test in the examples and controls of the present invention are shown in Table 1. The methods used for testing the properties are as follows.

[0013]

(1) Measurement of the melting point (the liquidus and the solidus)

The alloys as examples and controls are put into an electric furnace with an atmosphere of argon gas to be melted and the melting point is measured by a heat analysis method. According to this method, a thermocouple is put into the center of the melted alloy, the thermocouple connected to a recorder for drawing a heat analysis curve by which the temperatures of the liquidus and the solidus may be read.

[0014]

(2) Brazing test

The alloys as examples and controls are put into an electric furnace with an atmosphere of argon gas to be melted and thereby melted alloys are cast into a mold of graphite to obtain a rod having 5 mm in diameter. Then, the rod is

cut into a sample of fine fragment, each fragment having about 5 mm in length. Then, the obtained sample is put on a base material of SUS 304 stainless steel, as shown in Fig. 1(a), and the sample is heated at 1050°c for 30 minutes in a vacuum atmosphere of 10^{-4} to 10^{-3} torr for brazing. After brazing, the area S is measured into which the melted sample spreads, as shown in Fig. 1(b). The measured area S is divided by the cross sectional area So of the sample before brazed to obtain a spread coefficient W of the melted alloy in brazing, namely S/So, which may provide a useful estimation for the wettability toward the base material of SUS 304 stainless steel.

[0015]

(3) The salt-water spray test of the sample by a brazing test

A salt-water spray test in accordance with JISZ 2371 "the salt water spray test method" was carried out on the sample after the above described brazing test. The generation of rust in the interface of the brazing alloy surface and the base material was carefully observed. The observation result provides a useful index of a salt-water corrosion resistance. The test was carried out for 48 hours (observation was made every 6 hours) and if generation of rust was not observed after 48 hours, the sample was estimated as "good." In addition, because the samples of the control examples of No. a, b, c and e provided poor result of brazing at 1050°C, the salt-water

spray test was not carried out for those samples. Moreover, as for BNi-5, the salt-water spray test was carried out for the sample brazed at 1200°C.

[0016]

As shown in Table 1, it is apparent that all the alloys of the example of the present invention have no less than 40 of spread coefficients and a good wettability to a SUS304 stainless-steel base material in a 1050°C brazing test. Moreover, according to the result of the salt-water spray test, after 48 hours, generation of rust on the brazing alloy surface or on the interface with a base material was not observed for all the samples. It is apparent that the alloys of the example of the present invention showed a good salt-water corrosion resistance.

[0017]

On the other hand, the alloys of controls of No. a to e have a composition out of the range defined as the present invention. The alloy composition of No. a and b has a low solidus temperature, and they have a high liquidus temperature, and as a result they cannot be brazed at 1050°C. Since No. c has a high solidus temperature and a high liquidus temperature, it does not melt at 1050°C, and as a result it cannot be brazed at the temperature. Although No. d has a appropriate melting

point and can be brazed 1050°C, it has a poor salt water corrosion resistance originated in excessive content of P, and in insufficient content of Si. No. e, which has an excessive amount of Mo, has a high liquidus temperature, and as a result has a poor wettability with the stainless steel base material.

[0018]

On the other hand, in the alloy of a control, BNi-7, 5 and 2 are the Ni-base brazing alloy compositions specified in the conventional JIS. Although BNi-7 and BNi-2 have low melting points, and are brazed sufficiently at 1050°C, it was proved that they have a poor salt-water corrosion resistance based on an observation of red rust generation in less than 24 hours in the salt water spray test. BNi-5 cannot be brazed at 1050°C because it has a high melting point. In addition, according to the present invention, the alloy has an excellent wettability not only to stainless steel base material of austenite such as SUS 304 and 316 but also to stainless steel base material of ferrite and martensite such as SUS 410 and 430. The present alloy may be preferably brazed not only in a vacuum atmosphere but also in a reductive atmosphere of hydrogen or in an inert atmosphere of argon.

[0019]

[Table 1]

	Alloy No.	Alloy composition (weight %)					Melting point (°C)		1050°C brazed spread coefficient W	The salt-water corrosion resistance of a brazed sample fragment
		Ni	Cr	P	Si	Mo	Solidus	Liquidus		
Example alloy	1	Remainder	13.5	9.7	1.1	-	882	940	>50	Good
	2	Remainder	15.0	7.6	3.4	-	877	980	>50	Good
	3	Remainder	16.0	5.4	5.7	-	945	1032	>50	Good
	4	Remainder	18.2	3.2	8.0	-	968	1058	40	Good
	5	Remainder	19.0	2.2	9.1	-	973	1068	40	Good
	6	Remainder	10.0	6.9	4.6	-	880	1018	>50	Good
	7	Remainder	15.0	6.9	4.6	-	877	1000	>50	Good
	8	Remainder	20.0	6.9	4.6	-	962	998	>50	Good
	9	Remainder	25.0	6.9	4.6	-	985	1010	>50	Good
	10	Remainder	30.0	6.9	4.6	-	988	995	>50	Good
	11	Remainder	15.0	8.0	2.0	-	885	1030	>50	Good
	12	Remainder	20.0	7.8	5.2	-	985	1050	50	Good
	13	Remainder	20.0	6.9	4.6	2.0	970	1008	>50	Good
	14	Remainder	20.0	6.9	4.6	5.0	977	1020	>50	Good
	15	Remainder	14.5	7.6	3.1	0.5	880	1006	>50	Good
	16	Remainder	15.7	5.4	5.2	3.3	868	1052	40	Good
Control alloy	a	Remainder	9.5	3.0	2.0	-	885	1310	3	Red rust in 24 hours
	b	Remainder	33.0	8.5	5.5	-	965	1170	5	
	c	Remainder	19.8	1.1	10.2	-	1072	1072	1	
	d	Remainder	14.5	11.5	0.5	-	886	930	>50	
	e	Remainder	20.0	6.9	4.6	6.8	980	1070	5	
	BNi-7	Remainder	12.7	10.8	-	-	880	905	>50	Red rust in 24 hours
	BNi-5	Remainder	18.7	-	10.4	-	1072	1160	1	(Good)[2)]
	BNi-2	Remainder	7.0	-	4.5	B:3.2 Fe:3.0	975	1010	>50	red rust in 6 hours

Notes)

1) salt spray test, after 48hr no red rust observed

2) 1200°C brazing sample fragment

[0020]

[Effects of the Invention]

As explained in full detail, the Ni-base brazing alloy of a the present invention has a low melting point, and the alloy can be brazed to the various stainless steel with a stable

oxide film formed on the surface at a low temperature of about 1050°C which is lower for conventional Ni-based brazing alloys. Moreover the alloy has an excellent wettability and at the same time an excellent corrosion resistance to salt-water.

[Brief Description of the Drawings]

[Fig. 1]

Fig. 1 is a schematic diagram describing a brazing test of a brazing alloy.

[Description of Reference Numerals]

So: The cross sectional area of a brazing material sample

S: Spread area of the alloy after brazed

W: Spread coefficient (S/So)

1: Base material (SUS304 stainless steel)

2: The brazing material sample before brazing (5 ϕ x about 5 mm)

3: The brazed material alloy spread after brazing